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Analysis of Technical Chlordane by Gas Chromatography Mass Spectrometry

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Analysis of Technical Chlordane by Gas Chromatography/Mass Spectrometry

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The composition of technical chlordane has been investigated by combined gas chromatography/mass spectrometry, employing a column commonly used for pesticide residue analysis. Partial or complete structure identifications have been assigned to some 45 individual constituents. Many of these compounds are simple Diels–Alder adducts of cyclopentadiene and hexachlorocyclopentadiene, with further chlorine addition or substitution. Additionally, a series of adducts derived from tetra- and pentachlorocyclopentadiene, followed by further chlorination, has been identified. Several components appear to have incorporated trichloromethyl moieties from the solvent during manufacture. Other compounds with abnormal or rearranged ring fusions have also been recognized and their unusual mass spectra have been studied.

Technical chlordane has been widely used for many years for control of termites, ants, and other insects in and around domiciles and institutions, as well as for agricultural pest control. The insecticide has remained in popular use in the U.S. until recent times, with nearly 10^7 kg produced for domestic and foreign use in 1974 (*1*). Consequently, large quantities of the material have been dispersed throughout the general environment. Residues related to technical chlordane have been reported in air (*2–4*), water (*5, 6*), soils (*7*), food products (*8–10*), the tissues of domestic animals and wildlife (*11, 12*), and the general human population of the U.S. (*13–15*).

Determination of chlordane residues in environmental and biological samples is complicated by the fact that the commercial pesticide is a complex mixture consisting of at least 11 major components. A listing of these components as supplied by the manufacturer to the U.S. Environmental Protection Agency (*16*) is given in Table I. The exact structures of several of these compounds have not yet been established. Furthermore, most of these compounds are readily metabolized or oxidized by biochemical or environmental action. Before meaningful correlations can be established between measured chlordane residues and actual environmental exposure, therefore, a thorough and accurate determination of the composition of technical chlordane must be made.

The production of technical chlordane begins with the Diels–Alder condensation of cyclopentadiene and hexachlorocyclopentadiene to yield a compound commonly called "chlordene" (structure I, Figure 1). Further chlorination under heat leads to the formation of a number of other *endo*-4,7-methanoindene compounds, which make up the major components of technical chlordane (*17, 18*). Substitution of chlorine into the allylic position 1 results in the production of heptachlor (structure II), which accounts for approximately 7% of the technical mixture. Addition of chlorine to the 2–3 double bond of I yields both α- and γ-chlordane (structures III and IV, respectively). These isomers are commonly considered to be the two major components of the mixture and are each reported by the manufacturer to be present in the amount of about 20% of the total weight (*19*).

Table I. Composition of Technical Chlordane as Supplied to the Environmental Protection Agency by the U.S. Manufacturer (*30*)

Component	Wt % total mixture
α-Chlordane (cis)	19 ± 3
γ-Chlordane (trans)	24 ± 2
Heptachlor	ca. 7
trans-Nonachlor	7 ± 3
"Isomer 2-Chlordene"	7.5 ± 2
α-Chlordene	ca. 3
β-Chlordene	ca. 4
γ-Chlordene	ca. 9
Chlordene	1 ± 1
Related compounds (including *cis*-nonachlor and compound "K"	19.5

However, recent studies indicate that they may constitute only half this amount (*20, 21*). Among the other significant components which have been identified (*19, 22–24*) in technical chlordane are *cis*- and *trans*-nonachlor (structures V and VI), which logically derive from chlorination of the 2–3 double bond of heptachlor (II).

A more complete analysis of technical chlordane has been conducted in our laboratories with the aids of combined gas chromatography/mass spectrometry and nuclear magnetic resonance spectroscopy. Identifications by GC/MS were carried out on a column commonly used for pesticide residue analysis and retention times relative to aldrin were determined.

EXPERIMENTAL

Materials and Standards. Technical chlordane was supplied by Velsicol Chemical Corp., Chicago, Ill. Two batches were examined: Lot No. 3316A, which was several years old, and Lot No. B8113, which was obtained in March 1975. Both batches were identical in all significant respects. All analytical standards of chlordane components were obtained from the manufacturer except for *cis*-nonachlor (V, Figure 1), which was provided by the Pesticides Tolerances Division, U.S. Environmental Protection Agency, Washington, D.C. Those obtained from Velsicol were chlordene (I); heptachlor (II); α-chlordane (III); γ-chlordane (IV); *trans*-nonachlor (VI); α-, β-, and γ-chlordene ($C_{10}H_6Cl_6$); β-dihydroheptachlor ($C_{10}H_7Cl_7$, mp 133–4 °C); compound "G" (reported by Velsicol to be $C_{10}H_7Cl_7$, mp 87–88.5 °C); compound "H" (reported by Velsicol to be $C_{12}H_8Cl_8$, mp 200–201 °C); and compound "K" ($C_{10}H_6Cl_8$, mp 119–121 °C). Purities were reported to be greater than 97% for each standard; therefore, no attempt was made at further purification. Melting points agreed with published values, where available. It was also necessary to synthesize several compounds for use as standards (see Results and Discussion).

All solvents used were Distilled-in-Glass (Burdick and Jackson, Muskegon, Mich.) or equivalent. All other chemicals were ACS reagent grade or better.

Gas Chromatography/Mass Spectrometry. Three instruments were employed in this study. Most analyses were performed on a Hewlett-Packard 5930A mass spectrometer equipped with a Model 5700A gas chromatograph and a Model 5932A data system. A 183 cm × 2 mm (i.d.) glass column packed with 1.5% OV-17/1.95% OV-210 on 80–100 mesh Gas-Chrom Q

MS-16-083

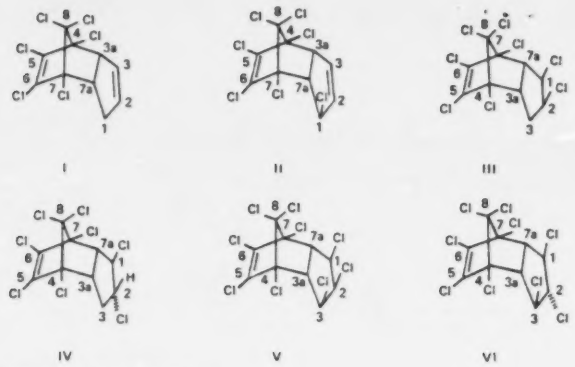

Figure 1. Structures I–VI

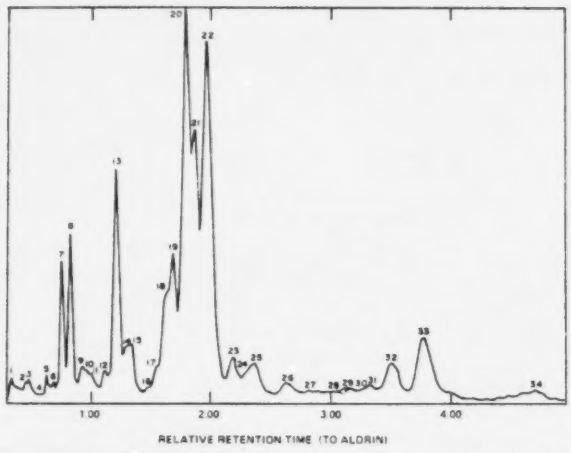

Figure 2. Reconstructed total ion chromatogram of technical chlordane

was used. The GC inlet temperature was 200 °C. Helium flow rate was 42 mL/min. Temperature programmed runs were made from 80 °C (2 min) to 210 °C at 8 °C/min. Isothermal runs were made at 180 or 190 °C. Selected ion monitoring of high mass components was carried out at 210 °C. The transfer line to the mass spectrometer was maintained at 210 °C and the silicone membrane separator was kept at 190 °C.

Quantitative determination of one component, *trans*-nonachlor (VI), was accomplished by selected ion monitoring employing a technique based on the use of a nonisotopically labeled internal standard. A solution of 5.08 mg/mL of technical chlordane and 0.50 mg/mL of *p,p'*-DDE (internal standard) in hexane was subjected to GC/MS analysis as described above, along with a standard solution containing 0.50 mg/mL each of VI and *p,p'*-DDE. The absolute intensities of the 409 m/e ion from VI and the 318 m/e ion from *p,p'*-DDE were measured and their ratios determined for each solution. The percentage of VI in the technical mixture can then be calculated from Equation 1:

$$\%\mathrm{VI} = \frac{r_i r_w}{r_i'} \frac{W_s}{W_c} 100 \qquad (1)$$

where r_i and r_i' are the ratios of the 409 to 318 ion intensities for the sample and standard, respectively; r_w is the weight ratio of VI to *p,p'*-DDE in the standard; and W_s and W_c are the weights of *p,p'*-DDE and technical chlordane in the sample, respectively. The concentration of VI in Lot. No. 3316A was thereby determined to be 5.18 ± 0.21% (standard deviation ± 0.35 for ten determinations), which is in agreement with the manufacturer's assay (*19*).

Chemical ionization mass spectra were obtained on a Finnigan 3200 mass spectrometer with a Model 6100 data system and a Model 9500 gas chromatograph. The same GC column mentioned above was operated isothermally at 210 °C. Methane was used as the reagent gas and was maintained at 1 mm in an ion source operated at 60 °C.

High-resolution mass spectrometry was carried out on a Varian MAT Model CH-5DF instrument equipped with a Model SS-100 data system and a Model 2700 gas chromatograph. A 183 cm ×

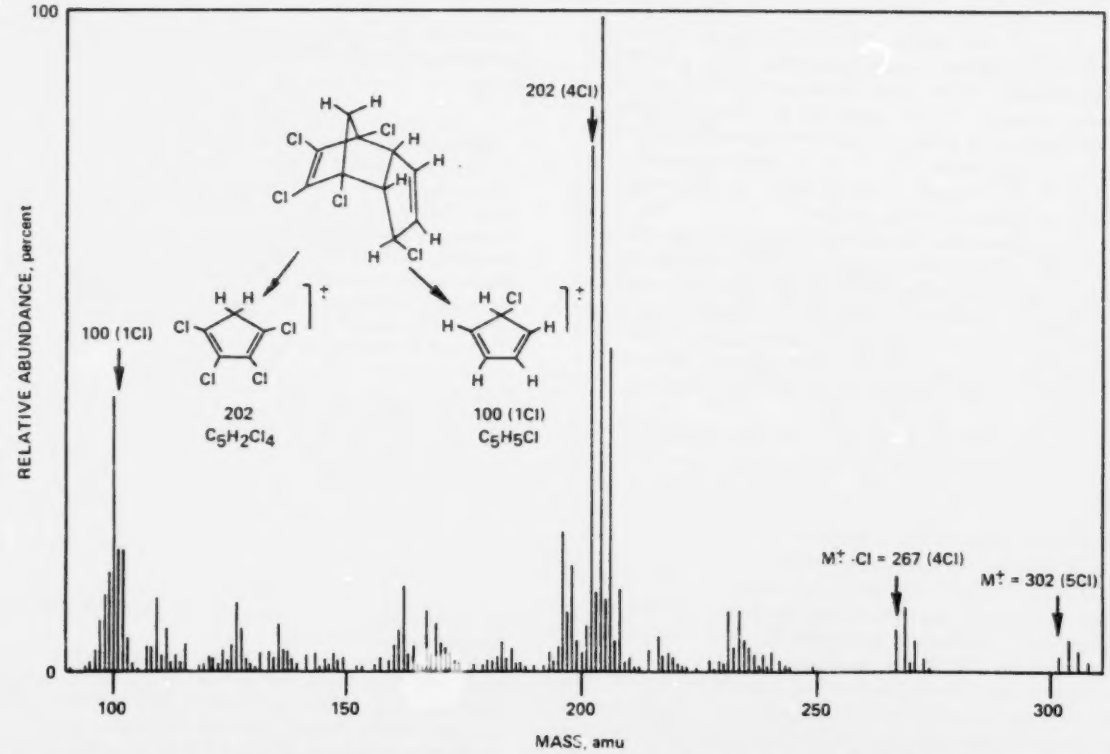

Figure 3. Mass spectrum of monochlorinated adduct of tetrachlorocyclopentadiene and cyclopentadiene. The mass spectrum does not indicate the unique structure shown, but is consistent with all adducts possible from the many isomers of tetrachlorocyclopentadiene

Galley AC1M1 DLD

Table II. Analysis of Technical Chlordane

GC peak No.	RRT_a[a]	Assigned mol wt	Assigned formula	Significant *m/e* (chlorine content)	Compd identity
		270	C_5Cl_6	270 (6 Cl), 235 (5 Cl)	Hexachlorocyclopentadiene[b,c]
		306	C_5HCl_7	306 (7 Cl), 271 (6 Cl), 235, 236 (5 Cl), 201 (4 Cl)	Heptachlorocyclopentene[b]
1	0.29	340	C_5Cl_8	340 (8 Cl), 305 (7 Cl), 270 (6 Cl), 235 (5 Cl)	Octachlorocyclopentene[b]
2	0.45	302	$C_{10}H_7Cl_5$	302 (5 Cl), 267 (4 Cl), 202 (4 Cl), 100 (1 Cl)	Monochloro adduct of tetrachlorocyclopentadiene with cyclopentadiene
3	0.49	302	$C_{10}H_7Cl_5$	302 (5 Cl), 267 (4 Cl), 231 (3 Cl), 202 (4 Cl), 100 (1 Cl)	Same as above
4	0.55	336	$C_{10}H_6Cl_6$	336 (6 Cl), 301 (5 Cl), 270 (6 Cl), 235 (5 Cl), 66	Chlordene[c]
5	0.63	302	$C_{10}H_7Cl_5$	267 (4 Cl), 266 (4 Cl), 231 (3 Cl), 196 (2 Cl)	A pentachlor which only gave $M^+ - Cl$, and $M^+ - HCl$
6	0.67	336	$C_{10}H_6Cl_6$	301 (5 Cl), 236 (5 Cl)	Chlordene isomer of the pentachlorocyclopentadiene series
7	0.74	336	$C_{10}H_6Cl_6$	336 (6 Cl), 301 (5 Cl), 265 (4 Cl), 236 (5 Cl), 230 (3 Cl), 196 (2 Cl), 100 (1 Cl)	Monochloro adduct of pentachlorocyclopentadiene with cyclopentadiene
8	0.81	370	$C_{10}H_5Cl_7$	370 (7 Cl), 335 (6 Cl), 300 (5 Cl), 299 (5 Cl), 270 (6 Cl), 264 (4 Cl), 230 (3 Cl), 100 (1 Cl)	Heptachlor[c]
9	0.91	336	$C_{10}H_6Cl_6$	301 (5 Cl), 202 (4 Cl)	α-Chlordene[c] and possible chlordene isomer of the tetrachlorocyclopentadiene series
10	0.94	336	$C_{10}H_6Cl_6$	301 (5 Cl)	Isomer of chlordene
11	0.97	302	$C_{10}H_7Cl_5$	267 (4 Cl), 230 (3 Cl), 196 (2 Cl), 100 (1 Cl)	Pentachlor with chlorocyclopentadiene fragment
12	1.11	370	$C_{10}H_5Cl_7$	335 (6 Cl), 300 (5 Cl), 236 (5 Cl)	Heptachlor isomer of the pentachlorocyclopentadiene series
13	1.22	336	$C_{10}H_6Cl_6$	336 (6 Cl), 301 (5 Cl), 265 (4 Cl), 230 (3 Cl), 196 (2 Cl), 169 (3 Cl)	β-Chlordene[c] and γ-chlordene[c]
14	1.28	370	$C_{10}H_5Cl_7$	335 (6 Cl), 299 (5 Cl)	Heptachlor isomer
	1.29	406	$C_{10}H_6Cl_8$	371 (7 Cl), 270 (6 Cl)	Chlordane isomer derived from hexachlorocyclopentadiene
	1.29	372	$C_{10}H_7Cl_7$	337 (7 Cl), 236 (5 Cl)	Dihydroheptachlor isomer, possibly of the pentachlorocyclopentadiene series
15	1.33	406	$C_{10}H_6Cl_8$	406 (8 Cl), 371 (7 Cl), 236 (5 Cl)	Chlordane isomer of pentachlorocyclopentadiene series
16	1.49	336	$C_{10}H_6Cl_6$	301 (5 Cl), 202 (4 Cl), 265 (4 Cl)	Chlordene isomer of the tetrachlorocyclopentadiene series
17	1.55	338	$C_{10}H_8Cl_6$	303 (5 Cl), 267 (4 Cl)	Dihydrochlordene isomer
18	1.65	372	$C_{10}H_7Cl_7$	337 (6 Cl), 301 (5 Cl), 265 (4 Cl), 266 (4 Cl), 236 (5 Cl), 201 (4 Cl)	Dihydroheptachlor isomer[c] of the pentachlorocyclopentadiene series (designated as compound "G" by the manufacturer)
19	1.67	370	$C_{10}H_5Cl_7$	370 (~7 Cl), 335 (~6 Cl), 270 (6 Cl)	Heptachlor isomer (minor component)
	1.68	440	$C_{10}H_5Cl_9$	405 (8 Cl)	Nonachlor isomer
20	1.80	406	$C_{10}H_6Cl_8$	406 (8 Cl), 371 (7 Cl), 335 (6 Cl), 229 (5 Cl)	*trans*-Chlordane[c]
21	1.86	440	$C_{10}H_5Cl_9$	440 (9 Cl), 405 (8 Cl), 369 (7 Cl), 270 (6 Cl), 235 (5 Cl)	*trans*-Nonachlor[c,d]
22	1.96	406	$C_{10}H_6Cl_8$	406 (8 Cl), 371 (7 Cl), 335 (6 Cl), 270 (6 Cl), 235 (5 Cl)	*cis*-Chlordane[c]

23	2.18	454	$C_{11}H_4Cl_9$	419 (8 Cl)	Possible ($Cl_3C\cdot$ + H) adduct to chlordene
		372	$C_{10}H_7Cl_7$	337 (6 Cl)	Dihydroheptachlor isomer[c] (designated as compound "H" by the manufacturer)
24	2.35	474	$C_{10}H_4Cl_{10}$	439 (9 Cl)	Decachlor isomer
25	2.32	406	$C_{10}H_6Cl_8$	371 (7 Cl)	Chlordane isomer
26	2.66	406	$C_{10}H_6Cl_8$	373 (partial 7 Cl), 335 (6 Cl),	Chlordane isomer
27	2.69	372	$C_{10}H_7Cl_7$	337 (6 Cl), 270 (6 Cl)	Dihydroheptachlor isomer
28	2.86	406	$C_{10}H_6Cl_8$	371 (7 Cl, partial cluster)	Chlordane isomer
	3.13	372	$C_{10}H_7Cl_7$	337 (6 Cl), 202 (4 Cl)	Dihydroheptachlor isomer of the tetrachlorocyclopentadiene series
		440	$C_{10}H_5Cl_9$	409 (partial 8 Cl)	Nonachlor isomer
29	3.17	372	$C_{10}H_7Cl_7$	337 (6 Cl)	Dihydroheptachlor isomer
30	3.33	488	$C_{11}H_6Cl_{10}$	488 (10 Cl), 453 (9 Cl)	Possible $Cl_3C\cdot$ + $Cl\cdot$ adduct to chlordene
31	3.38	440	$C_{10}H_5Cl_9$	405 (8 Cl)	Nonachlor isomer
		372	$C_{10}H_7Cl_7$	337 (6 Cl)	Indication of dihydroheptachlor isomer
32	3.54	440	$C_{10}H_5Cl_9$	440 (9 Cl), 405 (8 Cl), 270 (6 Cl)	*cis*-Nonachlor[c]
33	3.79	406	$C_{10}H_6Cl_8$	406 (8 Cl), 371 (7 Cl), 335 (6 Cl), 214 (4 Cl)	Chlordane isomer[c] (designated as compound "K" by the manufacturer)
34	4.69	406	$C_{10}H_6Cl_8$	373 (partial 7 Cl), 335 (6 Cl)	Isomer of chlordane

[a] Retention time relative to aldrin (=1.00) at 180 °C. [b] Early eluting compounds identified in temperature-programmed analysis. [c] Analytical standard available for comparison. [d] Determined by selective ion monitoring to constitute 5.18 ± 0.21% of technical chlordane, Lot No. 3316A.

3 mm (i.d.) glass column packed with 3% Dexsil 300 on 80- to-100-mesh Chromosorb W and programmed from 100 to 240 °C at 5 °C/min was used. Direct analysis of daughter ions and first field free region defocusing were applied for detailed mass spectrometric analyses of one component (compound "K") of technical chlordane (25).

Samples of technical chlordane were analyzed in amounts ranging from 1 to 10 μg in order to obtain mass spectra of diagnostic quality for minor components. Aldrin was used as the internal standard for relative retention time (RRT) measurements.

RESULTS AND DISCUSSION

The reconstructed total ion chromatogram of technical chlordane is shown in Figure 2. Individual mass spectra were examined for molecular ions (M^+) and for the more intense $M^+ - Cl$ fragment ions corresponding to any chlorinated dicyclopentadiene ($C_{10}H_{12}$) or dihydrocyclopentadiene ($C_{10}H_{14}$) with 0 to 12 or 14 chlorine-atom content, respectively. Thus, all possible compounds of these two series arising from either chlorine substitution and/or addition could be recognized. The components found in the mixture are listed in Table II with structural assignments and relative GC retention times. GC peak numbers refer to those shown in Figure 2.

Three compositions were detected from the series $C_{10}H_{12-n}Cl_n$ (pentachlor, chlordene, and heptachlor) and five from the series $C_{10}H_{14-n}Cl_n$ (dihydrochlordene, dihydroheptachlor, chlordane, nonachlor, and decachlor). Two or more isomers of most of these compositions were identified by their different GC retention times. It should be noted, however, that two or more isomers that yield identical or nearly identical mass spectra would be identified as one compound if they coeluted from the GC column. The 45 individual components of technical chlordane suggested by GC–MS analysis (see Table II), therefore, represent a minimum number.

In many cases, isomeric compositions could be distinguished through formation of fragments resulting from the retro-Diels–Alder (RDA) reaction (*26–28*). Cyclopentadiene and substituted cyclopentadiene fragments containing from 0 to 6 chlorine atoms were found at 66, 100, 202, 236, and 270 amu. Dichloro- and trichlorocyclopentadienyl fragments of masses 134 and 168 were not observed. RDA fragments were usually accompanied by prominent $M^+ - Cl$ ions, permitting assignment of molecular formulas even in those cases where the M^+ ion intensity was weak.

Intense ion currents corresponding to hexachlorocyclopentadiene fragments (C_5Cl_6, m/e 270) were associated with many technical chlordane components (e.g., *trans*-chlordane). Heptachlor gave very strong ions at m/e 270 and 100, which corresponded to the two major RDA fragments of the molecule. Compounds lacking the 2–3 olefinic bond, on the other hand, produced only the cyclopentadienyl fragments. Hence, isomers of chlordane and nonachlor did not afford abundant dichlorocyclopentene ($C_5H_6Cl_2$, m/e 136) and trichlorocyclopentene ($C_5H_5Cl_3$, m/e 170) ions, respectively.

Also found in the commercial mixture were six compounds characterized by the production of abundant ions of mass 236 with five chlorine atoms (pentachlorocyclopentadiene RDA fragment). The two major members of this series were found to be analogues of chlordene ($C_{10}H_6Cl_6$) and chlordane ($C_{10}H_6Cl_8$), first recognized by Saha and Lee (*29*). The other compounds had not been previously reported. In addition to the m/e 236 ion, the chlordene analogues afford a monochlorocyclopentadiene fragment at m/e 100. All of these compounds apparently derive from pentachlorocyclopentadiene contamination in the hexachlorocyclopentadiene used to manufacture technical chlordane. They most probably result from Diels–Alder condensation of pentachlorocyclopentadiene and cyclopentadiene, with subsequent chlorine substitution or addition.

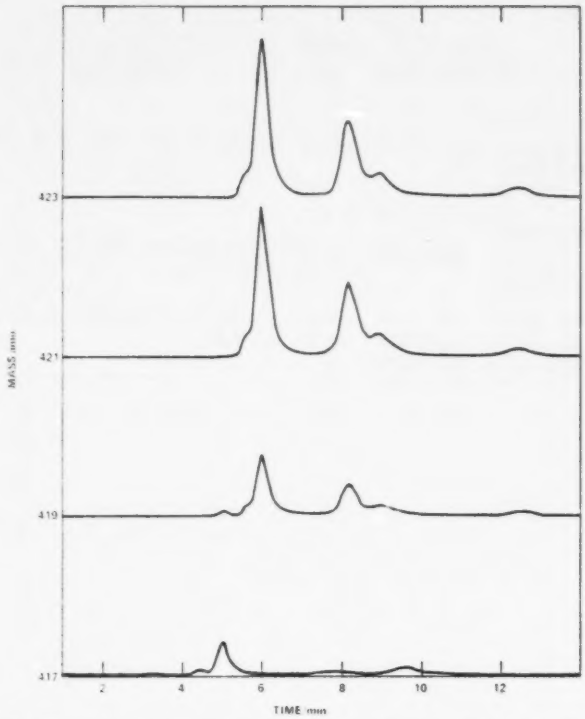

Figure 4. Selected ion monitoring of high mass components of technical chlordane. Column temperature: 210 °C. (The 417 *m/e* ion is shown to demonstrate that 419 *m/e* is the beginning of the $M^+ - Cl$ cluster)

A previously unrecognized series of compounds, characterized by the formation of intense tetrachlorocyclopentadiene fragments, was also identified in the technical mixture. The mass spectrum of one of these compounds, a monochlorinated adduct of tetrachlorocyclopentadiene and cyclopentadiene, is shown in Figure 3. The compound readily undergoes RDA fragmentation to $C_5H_2Cl_4$ (*m/e* 202) and C_5H_5Cl (*m/e* 100). These compounds likely originate from impurities in the hexachlorocyclopentadiene starting material. In addition, several other compounds identified in this study can be traced to the same starting material: hexachlorocyclopentadiene, heptachlorocyclopentene, and octachlorocyclopentene.

All of the chlordane components discussed above can be assigned molecular formulas and partial structures which are consistent with (1) substitution and/or addition of chlorine to chlordene, (2) logical neutral losses of Cl and HCl, and/or (3) RDA fragmentation of chlorocyclopentadiene adducts. It should be noted that the same RDA fragmentation patterns which arise from dienes such as chlordene (I) may derive from similar compounds containing a cyclopropane ring across the 1–3 position (*30*). However, previously unreported components were found which did not fit any of these categories. Isotope clusters beginning at *m/e* 419 and 453, which derive from compounds containing eight and nine chlorine atoms, respectively, were observed in the mass spectra. Exact mass measurements by high-resolution mass spectrometry indicated masses of 418.8058 and 452.7666 for the major components yielding these ions. Formulas $C_{11}H_7Cl_8$ and $C_{11}H_6Cl_9$ have calculated masses of 418.8056 and 452.7667, respectively, and may be assigned as $M^+ - Cl$ ions arising from $C_{11}H\text{-}Cl_9$ and $C_{11}H_6Cl_{10}$ (see Table III). Such compositions are best rationalized as deriving from the addition of a $Cl_3C\cdot$ radical to chlordene, followed by abstraction of H· or Cl· and possible subsequent rearrangement. Since $CHCl_3$ is used as a solvent in the preparation of technical chlordane (*31*), conditions may be favorable for formation of compounds of this series.

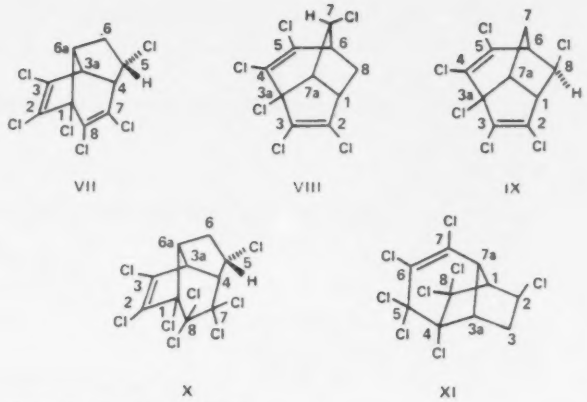

Figure 5. Structures VII–XI

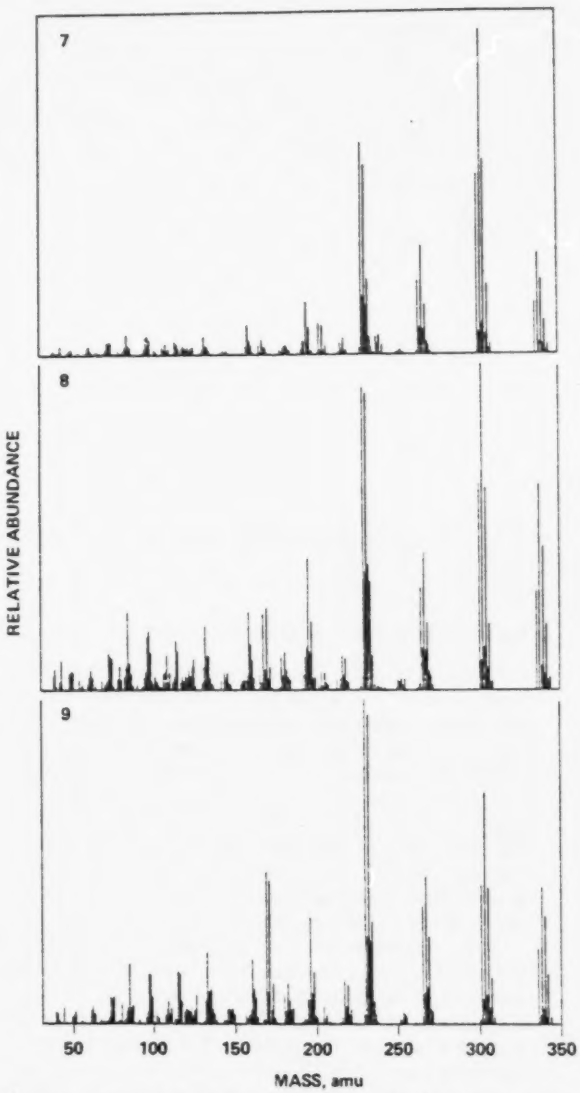

Figure 6. Mass spectra of α-, β-, and γ-chlordene (7, 8, and 9, respectively)

Selected ion monitoring (SIM) of the $M^+ - Cl$ cluster beginning at *m/e* 419 suggested that at least five overlapping species were present with molecular weight of 454 (see Figure 4). Similarly, at least two compounds of molecular weight

Table III. High-Resolution Mass Spectrometry of Selected Ions

Ion	Exptl mass	Calcd mass	Error, ppm	Assignment
m/e 419 ions from technical mixture (in order of elution)				
(1) Weak	418.7753			
(2) Intense	418.8058	418.8056	+0.48	$C_{11}H_7Cl_8$ (M^+ – Cl of $C_{11}H_7Cl_9$)
(3) Moderate	418.8037			
(4) Very weak	418.7995			
m/e 453 ions from technical mixture (in order of elution)				
(1) Intense	452.7320			
(2) Very intense	452.7666	452.7667	−0.22	$C_{11}H_6Cl_9$ (M^+ – Cl of $C_{11}H_6Cl_{10}$)
(3) Weak	452.7356			
(4) Weak	452.7621			
m/e 492 ion from technical mixture	491.7299	491.7296	+0.61	$C_{11}H_6{}^{35}Cl_8{}^{37}Cl_2$ (M + 4)
m/e 214 from compound "K"	213.8907	213.8911	−1.87	$C_6H_2Cl_4$
m/e 406 from compound "K"	405.7978	405.7978	0	$C_{10}H_6Cl_8$ (M^+)

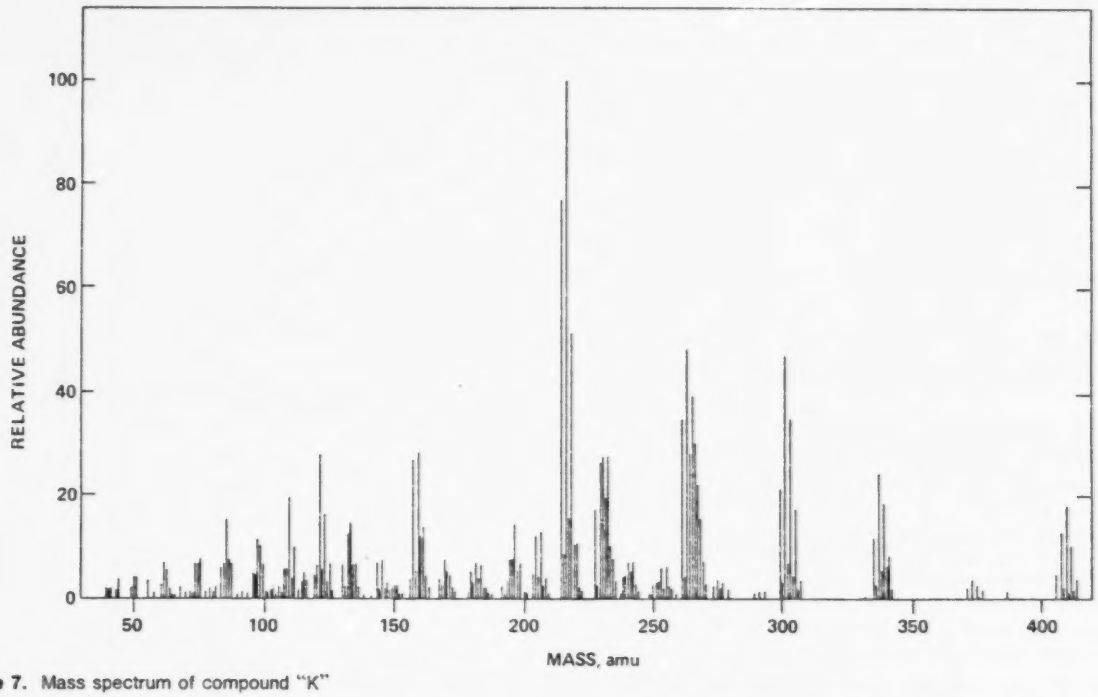

Figure 7. Mass spectrum of compound "K"

488 were detected. The structures of these high molecular weight compounds in this complex mixture have not yet been elucidated. Additional evidence of the complexity of technical chlordane can be seen from the range of exact mass measurements presented in Table III for lesser components of 419 and 453 nominal masses. Oxygenated compounds of the compositions $C_{10}H_3Cl_9O$ and $C_{10}H_2Cl_{10}O$ have been previously proposed (*30*) as possible precursors of the 419 and 453 fragment ions (M – Cl), respectively. However, high-resolution measurements now appear to eliminate such compounds as the major contributors to these masses.

Three important components of technical chlordane, which are isomeric with chlordene, have been recently determined not to be of the 4,7-methanoindene series (*24*, *32*, *33*). These compounds are commonly known as α-, β-, and γ-chlordene and have unusual ring fusions. Their structures are shown in Figure 5 as VII, VIII, and IX, respectively, and their mass spectra are shown in Figure 6. The absence of RDA fragmentation distinguishes them from other important constituents of technical chlordane. As can be seen, the mass spectra of β- and γ-chlordene are experimentally identical. Since the two compounds coelute from the GC column used in this study, the presence of both compounds in the technical mixture could not be demonstrated.

The component referred to as compound "K" by the manufacturer was of special interest because of its unusual mass spectrum (Figure 7). In contrast to most other chlordane constituents, the molecular ion (*m/e* 406) is more intense than the M^+ – Cl ion (*m/e* 371). The most prominent feature in the mass spectrum of compound "K" is the abundant odd-electron ion fragment at *m/e* 214, consistent with $C_6H_2Cl_4$. This composition was verified by high-resolution mass measurements (see Table III). Direct analysis of daughter ions (DADI) and metastable defocusing techniques demonstrated that the *m/e* 214 fragment originated directly from the molecular ion. Dechlorination of compound "K" with zinc and acetic acid yielded α-chlordene, suggesting structure X (Figure 5). However, critical interpretation of ^1H and ^{13}C NMR spectra favors structure XI (*33*), which could logically result from a Wagner–Meerwin rearrangement during the chlorination of α-chlordene. Rearrangement of XI to VII may also be expected to occur during dechlorination.

Investigation of the mass chromatograms and spectra of the components of technical chlordane also revealed a series of "reduced" chlordenes ($C_{10}H_5Cl_6$) and heptachlors ($C_{10}H_5Cl_7$). These components were originally suggested to arise from reduction of or HCl addition to the 2–3 double bond in chlordene (*34*). Standards of β-dihydroheptachlor and two

uncharacterized members of the reduced series, compound "G" and compound "H", were obtained from Velsicol Chemical Corp. for comparison with this series. Chemical ionization mass spectrometry demonstrated that both "G" and "H" have the molecular formula $C_{10}H_7Cl_7$, which is consistent with dihydroheptachlor compounds. Compound "G" undergoes RDA fragmentation to produce a prominent species at m/e 236 (5 Cl); hence, it appears to belong to the pentachlorocyclopentadiene-4,7-methanoindene series. On the other hand, "H" exhibits no discernible RDA fragmentation and may belong to the rearranged series (e.g., α-, β-, γ-chlordene). Both "G" and "H" were apparent in the technical mixture from our analyses and exhibit retention times relative to aldrin of 1.65 and 2.18, respectively.

There was no evidence, however, of a component identical to the β-dihydroheptachlor standard in the technical chlordane samples analyzed in our laboratory. For further confirmation, an isomeric mixture of α-, β-, and γ-dihydroheptachlor was synthesized from 1-chlordene by the procedure of Büchel et al. (*35*). Gas chromatographic analysis of the purified product revealed three components with RRT_{aldrin} of 0.98, 1.13, and 1.31. Mass spectra of each component were identical: 372 (M^+, weak), 337 (6 Cl, strong), 301 (5 Cl), 270 (6 Cl, strong), and 235 (5 Cl). The major component of the synthetic mixture was found to be identical with the standard of β-dihydroheptachlor furnished by the manufacturer. There was no indication from GC/MS of the presence of any of these isomers in technical chlordane.

Dihydrochlordene (4,5,6,7,8,8-hexachloro-4,7-methylene-3a,4,7,7,7a-tetrahydroindane) was synthesized by the method of Fechtinger et al. (*36*) and purified by column chromatography and recrystallization to 98.7%. Physical properties: mp 182–3 °C; IR (in CCl_4), 2975, 2898, 1604, and 1450 cm^{-1}; mass spectrum, 338 (M^+, 6 Cl, 5%), 303 (5 Cl, 29%), 270 (6 Cl, 58%), 267 (4 Cl, 32%), 235 (5 Cl, 40%), 68 (29%), and 67 (100%); RRT_{aldrin} = 0.69. The GC retention time of this compound did not match that of the isomer of dihydrochlordene found in the technical mixture (RRT_{aldrin} = 1.55). The isomer found in the mixture did not yield the RDA fragment ion at m/e 270; thus it apparently also belongs to the rearranged series.

No standard was available for the so-called "isomer 2-chlordene", although it is given as one of the major components of technical chlordane in the EPA Pesticides Standards Index (*16*). Therefore, the identity of this compound could not be confirmed. However, it is suspected to be the major member of the pentachlorocyclopentadiene series, corresponding to peak 7 in the total ion chromatogram of technical chlordane (see Figure 2).

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